Catalysts Surface with Tunable Hydrophilicity and Hydrophobicity: Metal-Organic Frameworks toward Controllable Catalytic Selectivity

Xinyi Chen[#], Panpan Qian[#], Tao Zhang, Zhiling Xu, Chuanzhen Fang, Xiujie Xu, Wanzheng Chen, Peng Wu, Yu Shen, Sheng Li, Jiansheng Wu, Bing Zheng, Weina Zhang*and Fengwei Huo*

Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, P.R. China.

E-mail: iamfwhuo@njtech.edu.cn

General information: All chemicals were purchased from Sigma-Aldrich and used as received unless otherwise noted. Transmission electron microscope (TEM) images were taken by JEOL JEM-2100Plus at an accelerating voltage of 200 kV. Scanning electron microscope (SEM) images were taken by JEOL JSM-7800F. X-ray diffraction (XRD) patterns of samples was performed in Smartlab (3 kW). Nitrogen adsorption isotherms of powder samples were measured with Quantachrome ASIQM0V002-5. Contact angles were recorded on KRUSS GmbH DSA1005. UVvisible spectra were recorded on SHIMADZU UV-1750. Gas Chromatography (GC) was recorded on Agilent Technologies 7890B.

Pt@UiO-66: DMF solution of benzendicarboxylic acid (BDC), and Pt NPs solution were mixed in the glass vial by sonication. DMF solution of $ZrCl_4$ and acetic acid were dispersed in the above solution by sonication, and then maintained at 120 °C for 24 h without stirring. After cooling down, solid was collected by centrifugation, washed with DMF (three times). The product was immersed in methanol for three days (replacing the soaking solvent every 24 h). After that, the solid was washed 3 times with methanol.

PVP-stabilized Pt NPs: PVP, methanol, and water solution of H_2PtCl_6 were mixed in a flask by refluxing for 3 h under air. Methanol was removed by rotary evaporator. The NPs were precipitated by acetone in solution. And then, the NPs were collected by centrifugation at 6000 rpm for 5 min. The sample was cleaned with chloroform and hexane to remove excessive free PVP.

Graphene oxide: Graphite powder and sodium nitrate were added into the concentrated sulphuric acid, and stirred in an ice bath. After that, potassium permanganate was slowly added to the above solution in the ice bath. The suspensions were stirred for more than 8 h in 32 °C. Water was added

dropwise to the above solution, and then heated up to 95 °C. The suspension was further diluted with warm distilled water, and then, added hydrogen peroxide. The mixture was washed with hydrochloric acid.

Pt@UiO-66@GO: Pt@UiO-66 was dispersed in distilled water by sonication. Then, graphene oxide solution was added and the mixture was stirred more than 6 h, and then, collected by filtration. The product was final handled by freeze-drying.

Pt@UiO-66@rGO: Pt@UiO-66 was dispersed in distilled water by sonication. Then, graphene oxide solution was added and the mixture was stirred more than 6 h. Subsequently, ascorbic acid solution was added and heated up to 80 °C for 2 h to reduce graphene oxide. The product was collected by centrifugation and vacuum dried.

Catalytic hydrogenation of olefins: Hydrogenation of olefins (1-hexene and tetraphenylethylene) was carried out in ethyl acetate solution in a static hydrogen atmosphere. A catalyst was dispersed in ethyl acetate solution and the residual air in the reactor was expelled by flushing hydrogen several times. And then, the mixture was sonicated to afford a homogeneous suspension. Olefin was then added in the mixture with magnetic stirring. The reaction progress was monitored by gas chromatograph.

Selective catalytic reduction of nitrobenzene (NB) and 4-nitrophenol (4-NP): For investigating the catalytic selectivity of catalysts, the reduction of 4-NP and NB was carried out in water in a static hydrogen atmosphere. In a typical procedure, catalysts was added into water in a reactor and loaded with an H₂ balloon on top. The residual air in the reactor was expelled by flushing hydrogen several times. And then, the mixture was sonicated to afford a homogeneous suspension. 4-NP (or

NB) was added in the mixture with magnetic stirring. The reaction progress was monitored by UV-Vis spectra.



Figure S1 (a) SEM image of Pt@UiO-66@GO; (b) TEM image of Pt@UiO-66@GO.



Figure S2 (a) SEM image of Pt@UiO-66@rGO; (b) TEM image of Pt@UiO-66@rGO.



Figure S3 Image of the obtained samples after different lengths of reduction time dispersed in a

water-ethyl acetate (1:1 v/v) biphasic solution.



Figure S4 TEM image of Pt NPs.



Figure S5 TEM images of (a) Pt@GO and (b) Pt@rGO.



Figure S6 High resolution TEM images and Pt nanoparticles size distribution of (a) Pt@UiO-66@GO and (b) Pt@UiO-66@rGO.



Figure S7 TEM image of (a) Pd@UiO-66@GO and (b) Pd@UiO-66@rGO.



Figure S8 TEM image of (a) Pt/3X@GO and (b) Pt/3X@rGO.



Figure S9 (a) TEM image of Pt@UiO-66@GO after hydrogenation of 4-nitrophenol. (b) SEM

image of Pt@UiO-66@GO after hydrogenation of 4-nitrophenol.



Figure S10 X-ray diffraction patterns of Pt@UiO-66@GO after hydrogenation of 4-nitrophenol.



Figure S11 (a) TEM image of Pt@UiO-66@rGO after hydrogenation of 4-nitrophenol. (b) SEM

image of Pt@UiO-66@rGO after hydrogenation of 4-nitrophenol.



Figure S12 X-ray diffraction patterns of Pt@UiO-66@rGO after hydrogenation of 4-nitrophenol.



Figure S13 (a) TEM image of Pt@UiO-66@GO after hydrogenation of nitrobenzene. (b) SEM

image of Pt@UiO-66@GO after hydrogenation of nitrobenzene.



Figure S14 X-ray diffraction patterns of Pt@UiO-66@GO after hydrogenation of nitrobenzene.



Figure S15 (a) TEM image of Pt@UiO-66@rGO after hydrogenation of nitrobenzene. (b) SEM

image of Pt@UiO-66@rGO after hydrogenation of nitrobenzene.



Figure S16 X-ray diffraction patterns of Pt@UiO-66@rGO after hydrogenation of nitrobenzene.



Figure S17 Size-selective hydrogenations of olefins catalyzed by Pt@UiO-66, Pt@UiO-66@GO and Pt@UiO-66@rGO.



Figure S18 (a) TEM image of Pt@UiO-66@GO after hydrogenation of 1-hexene. (b) X-ray diffraction patterns of Pt@UiO-66@GO after hydrogenation of 1-hexene.



Figure S19 (a) TEM image of Pt@UiO-66@rGO after hydrogenation of 1-hexene. (b) X-ray diffraction patterns of Pt@UiO-66@rGO after hydrogenation of 1-hexene.

NMR Results







Author Contributions

X.Y Chen and P.P. Qian designed experiments, performed, analyzed the results, and drafted the manuscript. T. Zhang and Z.L. Xu were responsible for part of synthesis of graphene. C.Z. Fang and W.Z. Chen were responsible for part of the SEM characterization. X.J. Xu was responsible for part of the PXRD characterization. P. Wu and Y. Shen was responsible for part of the TEM characterization. Dr. Zheng, Dr. Li and Dr. Wu helped to revise the manuscript. Professor W.N. Zhang and Professor F.W. Huo supervised the project, helped design the experiments, and revised the manuscript. All authors contributed to the analysis of the manuscript.